



## **Analysis of Carbon and Sulfur in Steel Samples Using Bench Top Laser-Induced Breakdown Spectroscopy (LIBS)**

**by Frank C. De Lucia, Jr., Jennifer L. Gottfried, and Andrzej W. Miziolek**

**ARL-TR-5000**

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**Weapons and Materials Research Directorate, ARL**

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## Contents

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|   |           |
|---|-----------|
| <b>List of Figures</b>                              | <b>iv</b> |
| <b>List of Tables</b>                               | <b>iv</b> |
| <b>1. Introduction</b>                              | <b>1</b>  |
| <b>2. Experimental</b>                              | <b>1</b>  |
| <b>3. Results and Discussion</b>                    | <b>3</b>  |
| <b>4. Conclusions</b>                               | <b>8</b>  |
| <b>5. References</b>                                | <b>9</b>  |
| <b>List of Symbols, Abbreviations, and Acronyms</b> | <b>11</b> |
| <b>Distribution List</b>                            | <b>12</b> |

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## List of Figures

---

|  |   |
|--|---|
| Figure 1. LIBS spectra (single pulse, CCD spectrometer) of Benet Laboratories samples 1–14 (red) and 4130 steel (blue). Several argon and iron lines saturate the detector.....            | 2 |
| Figures 2a, 2b. LIBS spectra of Benet Laboratories samples and steel standards (a) region of strongest titanium atomic emission and (b) region of strongest chromium atomic emission. .... | 5 |
| Figure 3. LIBS spectra of steel standards and organic residue reference in regions of carbon atomic emission. ....   | 6 |
| Figure 4. LIBS spectra from the high resolution echelle spectrograph. ....   | 7 |
| Figure 5. LIBS spectra of 4130 steel and sulfur powder. ....   | 8 |

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## List of Tables

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|  |   |
|--|---|
| Table 1. Percentage of minor constituent elements in NIST steel standards..... | 2 |
| Table 2. The $r^2$ value for each sample with each steel standard. ....        | 3 |

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## 1. Introduction

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The need to analyze steel samples for their chemical composition is important for process control. Most methods currently employed generally require multiple sample preparation steps and off-site analysis. Laser-induced breakdown spectroscopy (LIBS) requires no sample preparation, can simultaneously detect all elements, can be configured as a portable system (1–4) and can be used for real-time online steel analysis (5–9). Recently, Benet Laboratories was interested in seeing if LIBS could be used to determine slight discrepancies in the composition of steel parts, such as trace amounts of carbon. LIBS analysis of carbon in steel samples typically involves using atomic emission lines in the vacuum ultraviolet (VUV) region (10–18). Collecting emission in the VUV usually involves using specialized spectrometers and sample chambers in order to avoid absorption of the plasma emission due to the O<sub>2</sub> Schumann-Runge band system (19). Also, the optics need to transmit light emission below 200 nm. Benet Laboratories provided several steel samples to the U.S. Army Research Laboratory (ARL) to see if a simple benchtop LIBS system could be used to detect carbon and sulfur emission in the 230–1000 nm ultraviolet-visible-near infrared (UV-VIS-NIR) range, in order to avoid using the specialized equipment needed to collect emission in the VUV. We also needed to confirm that the samples provided were 4130 steel.

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## 2. Experimental

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The ARL benchtop LIBS system utilized a 300 mJ laser pulse from a Nd:YAG laser (Big Sky Laser, Quantel, CFR 400). The laser was focused by a convex lens (100 mm) through a pierced mirror onto the sample surface, creating a microplasma. An argon flow was directed across the plasma in order to enhance the signal further. The plasma emission was collected by a parabolic mirror and focused onto a seven fiber optic bundle where it was delivered to a seven channel charge-coupled device (CCD) spectrometer (Ocean Optics, LIBS2500+). The gate delay was 1.25  $\mu$ s with a 1 ms integration time. We also used a double pulse Nd:YAG laser (Continuum, Surelite I-PIV) at 320 mJ per pulse for additional analysis. The laser pulses (separated by 1  $\mu$ s) passed through a flat pierced mirror and were focused by a 100 mm convex lens onto the sample surface. The plasma emission was collected by the lens and redirected by the flat mirror to a convex lens (50 mm) that focused the light onto a single 400  $\mu$  fiber. The fiber delivered the light to an echelle spectrograph (EMU-65, Catalina Scientific Instruments) with an electron multiplying charge-coupled device (EMCCD) (Andor iXon). The gate delay was 1.5  $\mu$ s with an integration time of 50  $\mu$ s. The echelle provided much higher resolution and dynamic range than the seven channel CCD spectrometer.

Ten LIBS spectra were collected from each Benet Laboratories sample (no. 1, no. 2, no. 4, no. 5, no. 6, no. 8, no. 9, no. 10, no. 11, no. 12, no. 13, no. 14, and two base plate samples) and from various National Institute of Standards and Technology (NIST) steel standards, including 4130 steel, a low alloy steel (1761a), and a stainless steel (C1296) using the single pulse laser system and the seven channel spectrometer. Ten additional spectra of the 1761a steel standard were collected using the double pulse system and the higher resolution echelle spectrometer. Table 1 lists the minor constituent elements discussed in this report for each steel standard. For every sample (NIST standards and Benet samples) the first spectrum was removed from the data set as it was primarily used to clean the surface of any contaminants. The remaining spectra were used to calculate an average LIBS spectrum for each of the samples and standards.

Table 1. Percentage of minor constituent elements in NIST steel standards.

|                 | <b>4130<br/>(%)</b> | <b>1761a<br/>(%)</b> | <b>C1296<br/>(%)</b> |
|-----------------|---------------------|----------------------|----------------------|
| <b>Carbon</b>   | 0.274               | 1.05                 | 0.038                |
| <b>Sulfur</b>   | 0.014               | 0.037                | 0.013                |
| <b>Chromium</b> | 0.91                | 0.222                | 27.9                 |
| <b>Titanium</b> | —                   | 0.173                | 0.23                 |

The numbered samples and the 4130 steel sample are displayed in figure 1. The spectra are all very similar as expected since the majority of the atomic emission lines in the 200–500 nm region are due to iron atomic emission. The largest atomic emission lines from 600–950 nm are due to the argon bath gas.

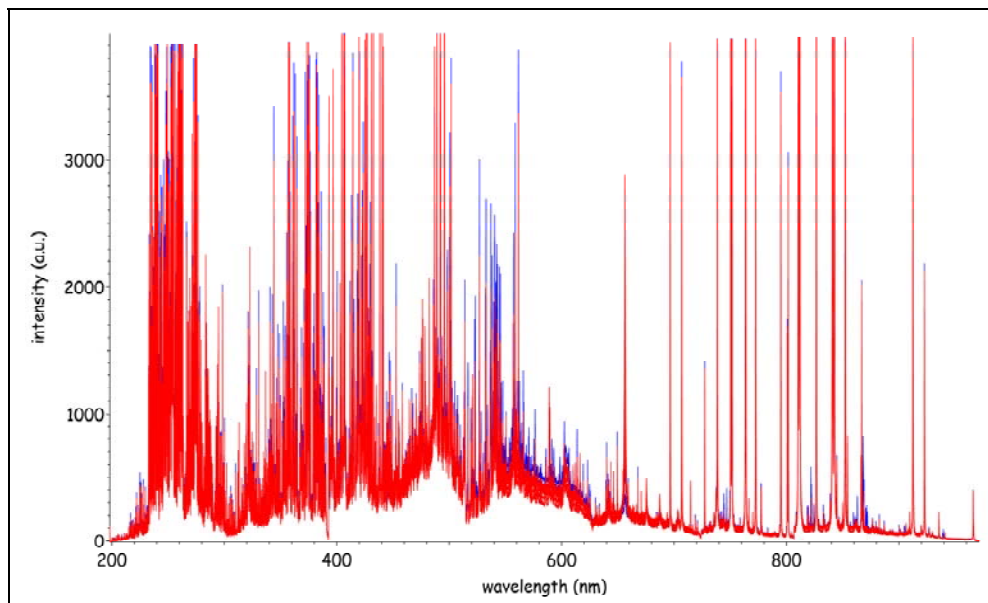


Figure 1. LIBS spectra (single pulse, CCD spectrometer) of Benet Laboratories samples 1–14 (red) and 4130 steel (blue). Several argon and iron lines saturate the detector.



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### 3. Results and Discussion

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We used linear correlation to determine if the Benet Laboratories samples were in fact 4130 steel. Each individual numbered sample spectrum and the base plate spectra were correlated against each individual spectrum from the NIST steel standards (4130 steel, 1761a, and C1296) to determine the  $r^2$  value from the Pearson correlation coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}. \quad (1)$$

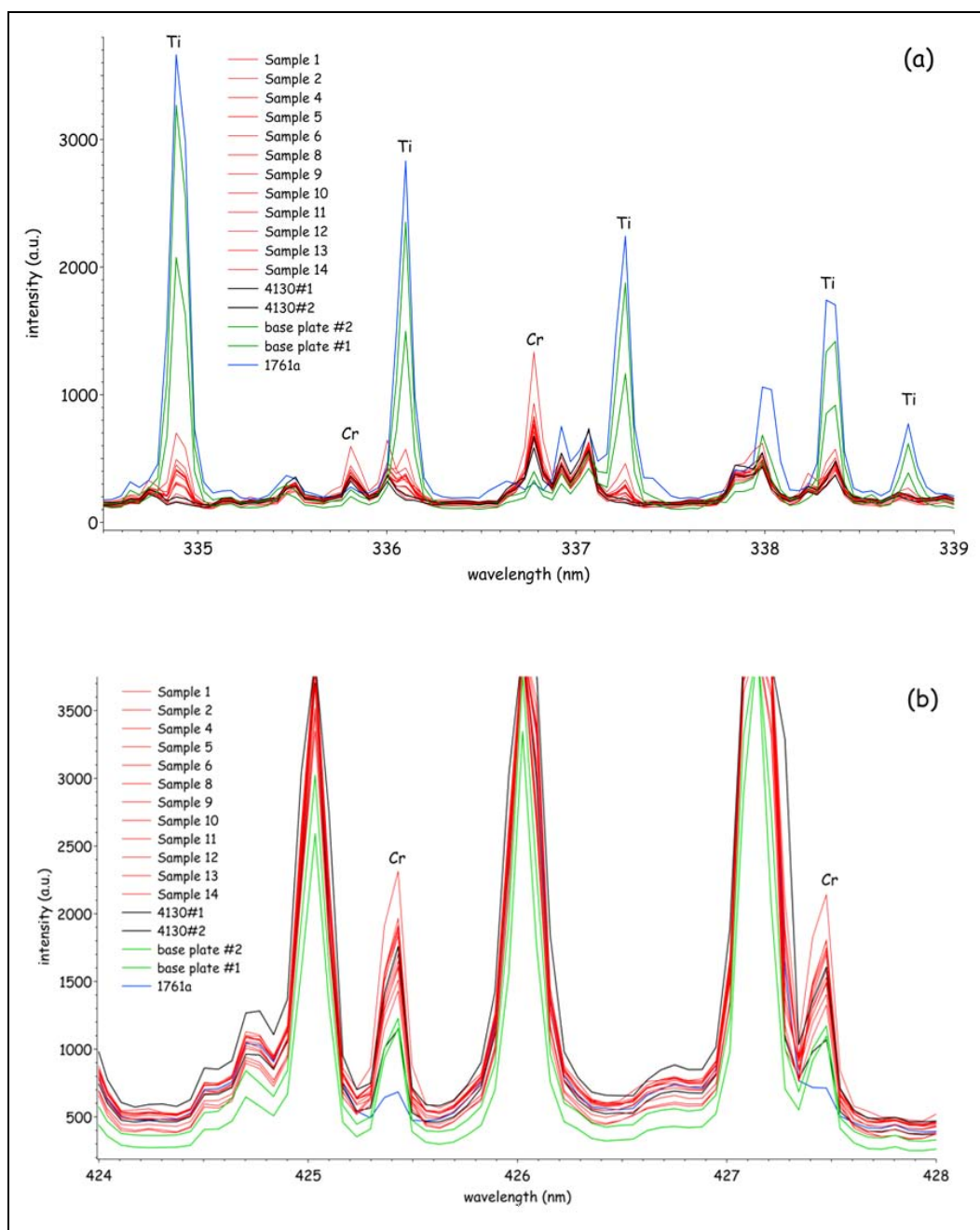
The  $r^2$  value is used as a measure of the association between two spectra, where  $r^2 = 1$  indicates that the spectra are identical. We correlated each of the nine spectra from each sample from Benet Laboratories with each of the nine spectra from the three steel standards. There were a total of 81 correlation coefficients calculated for each sample. The average correlation is calculated for each sample and the error is determined for a 95% confidence limit. The correlation for each sample was closest to the 4130 steel and the 1761a steel. The samples do not correlate with C1296 at all. Table 2 shows the comparison of the correlations between the two standards. Overall, the majority of the samples correlate more closely with the 4130 steel. However, the correlation is extremely close for the two standards. Since the majority of each standard consists of iron it is not surprising that the numbered samples closely correlate with both standards. In order to definitively determine the best match, closer inspection of minor atomic emission peaks is necessary. The 1761a alloy contains titanium (0.173%), unlike the 4130 steel standard. Prominent titanium atomic emission lines occur at 334.885, 336.099, 337.262, and 338.325 nm.

Table 2. The  $r^2$  value for each sample with each steel standard.

|              | 4130        | 1761a       | C1296       |
|--------------|-------------|-------------|-------------|
| Sample       | $r^2$ value | $r^2$ value | $r^2$ value |
| 1            | 0.968±0.004 | 0.955±0.003 | 0.719±0.005 |
| 2            | 0.963±0.005 | 0.949±0.004 | 0.748±0.006 |
| 4            | 0.959±0.004 | 0.946±0.003 | 0.729±0.004 |
| 5            | 0.939±0.007 | 0.938±0.006 | 0.714±0.006 |
| 6            | 0.957±0.004 | 0.951±0.004 | 0.736±0.005 |
| 8            | 0.965±0.007 | 0.953±0.006 | 0.715±0.004 |
| 9            | 0.959±0.004 | 0.952±0.003 | 0.714±0.005 |
| 10           | 0.955±0.008 | 0.945±0.007 | 0.725±0.005 |
| 11           | 0.897±0.014 | 0.895±0.012 | 0.721±0.006 |
| 12           | 0.973±0.003 | 0.963±0.001 | 0.723±0.004 |
| 13           | 0.953±0.008 | 0.946±0.006 | 0.727±0.005 |
| 14           | 0.908±0.008 | 0.918±0.007 | 0.713±0.005 |
| Base plate 1 | 0.779±0.014 | 0.805±0.013 | 0.647±0.011 |
| Base plate 2 | 0.824±0.011 | 0.846±0.009 | 0.668±0.010 |

In figure 2a, one can see that the numbered samples and the 4130 steel standard do not have prominent titanium lines compared to 1761a. However, the base plate samples clearly have higher titanium emission lines, thus higher titanium content. At 335.808 and 336.778 nm atomic emission lines due to chromium are much more prevalent in the numbered samples and the 4130 steel compared to the 1761a standard and the base plate. The chromium content in 4130 steel and the 1761a standard is 0.91% and 0.222%, respectively. Again, the more prominent chromium peaks indicate that the numbered samples are 4130 steel. Figure 2b shows the most prominent chromium lines at 425.43 and 427.476 nm; the numbered samples and the 4130 steel have the highest emission due to chromium. The two base plate samples have higher chromium emission than the 1761a standard. From the correlations and the peak analysis, it is evident that the numbered samples are 4130 steel. However, the two base plate samples have higher titanium content and lower chromium content than 4130 steel and do not match well with the 1761a or C1296 steel. It should be noted that these are results from a limited study. Further investigation could involve selecting the key minor element emission peaks (not iron peaks) in 4130 steel. These same peaks would be selected in a variety of steel standards (more than used in this study) and these emission intensities would be used as inputs for a variety of chemometric techniques; principal components analysis, partial least squares, and partial least squares discriminant analysis, etc. By using more steel standards and minor emission lines particular to 4130 steel in the model, the matching of unknown samples to 4130 steel would be more robust.

The spectrometer wavelength ranges available at ARL cover from 200–1000 nm. In this range the most prominent carbon line is at 247.8 nm. Other lines observed in organic samples are at 833.515, 909.483, and 940.573 nm. Figure 3 displays the LIBS spectra from the 4130 steel, the 1761a standard (has the highest % carbon content) and a residue of an organic material as a carbon reference. There was no carbon atomic emission at 833.515, 909.483, and 940.573 nm in any of the numbered samples or the standards as shown in figure 3. Unfortunately, an iron atomic line emits ~247.8 nm, interfering with any carbon emission that may be present. An attempt at generating a calibration line based on the intensity at 247.8 nm was still made using several carbon containing metal standards despite the potential interference. However, there was no linear correlation between the peak intensity and the known carbon concentration, indicating that the majority of the emission line in the spectra is due to the iron.



Figures 2a, 2b. LIBS spectra of Benet Laboratories samples and steel standards (a) region of strongest titanium atomic emission and (b) region of strongest chromium atomic emission.

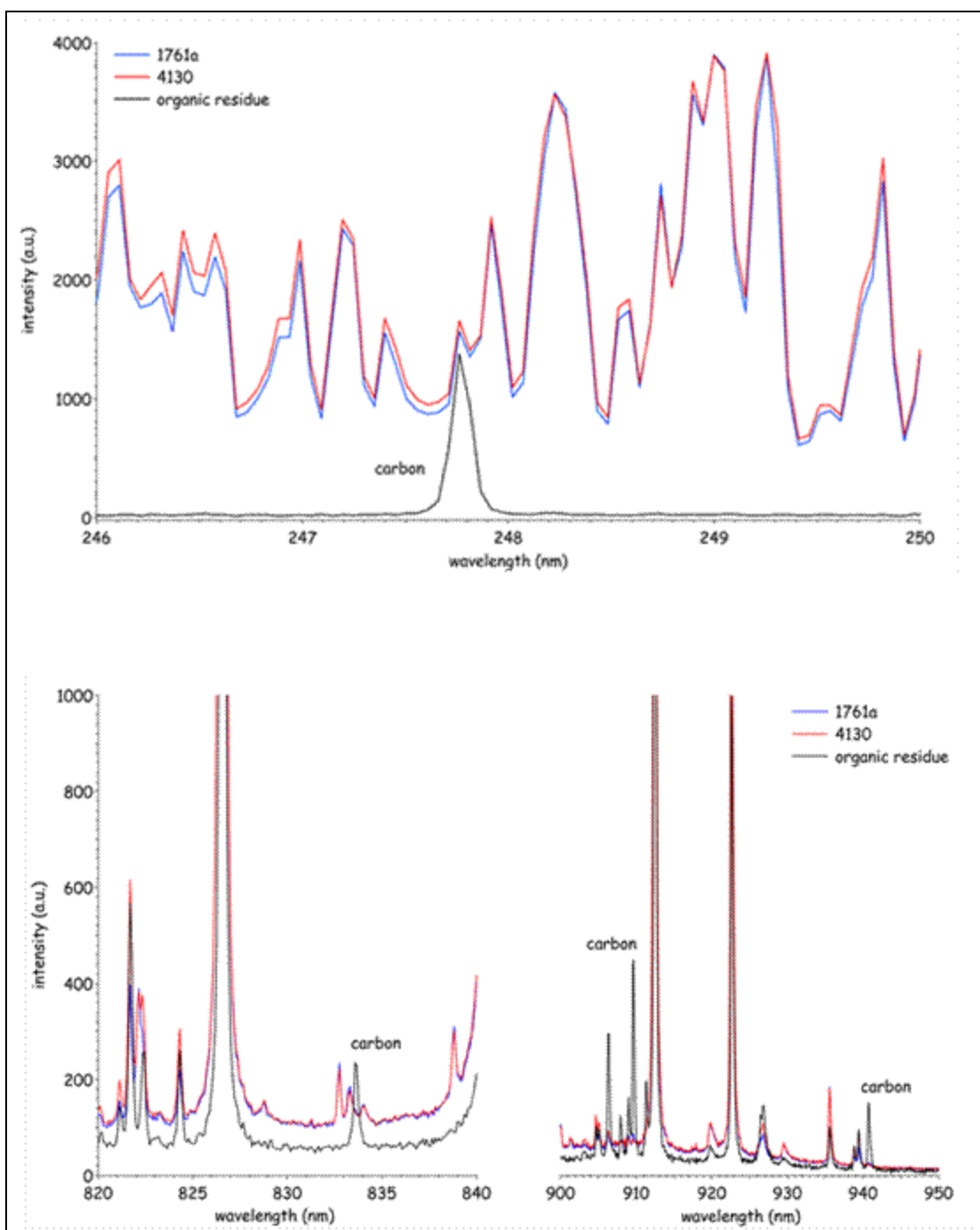


Figure 3. LIBS spectra of steel standards and organic residue reference in regions of carbon atomic emission.

We collected more LIBS spectra using the double pulse laser and the echelle spectrograph to improve the resolution. Figure 4 displays the spectra of the 1761a standard and the organic residue. We observe that the two peaks at ~248 nm do not overlap using the higher resolution spectrograph, further supporting the conclusion that the line in the steel standard is due to iron and not carbon. If any carbon emission is present then it is convoluted with the more prominent iron emission, making calibration all but impossible.

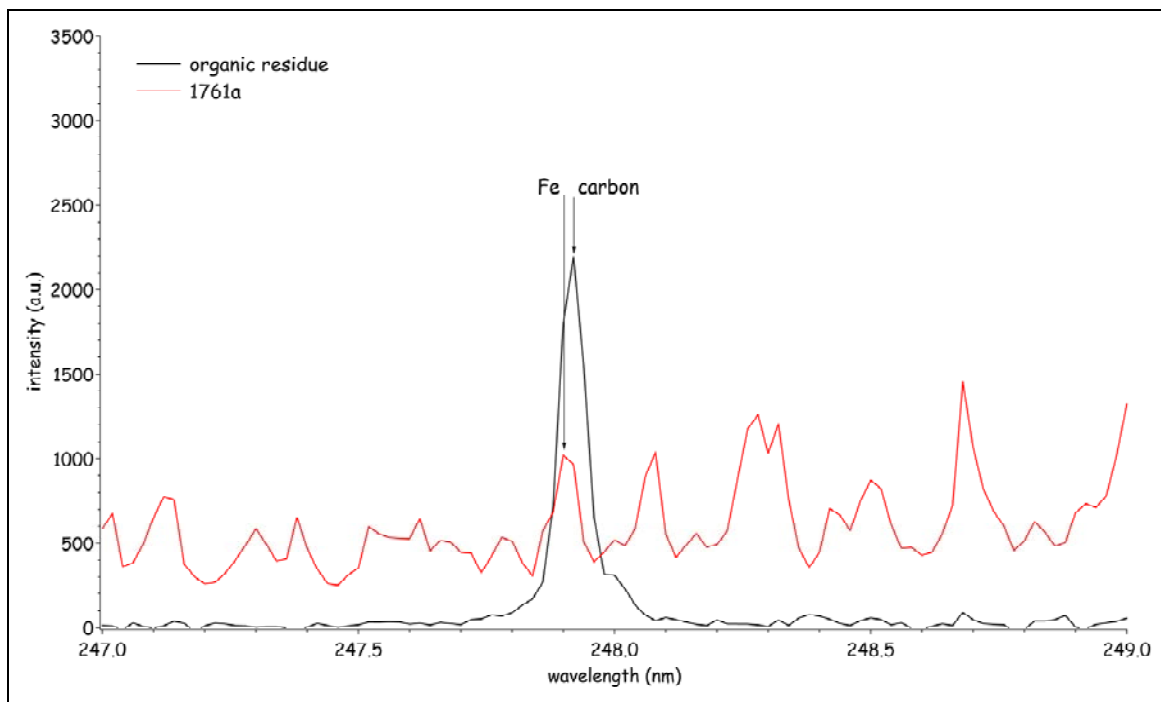


Figure 4. LIBS spectra from the high resolution echelle spectrograph.

The prominent sulfur emission lines in the ranges covered are observed at 869.47, 921.29, 922.81, and 923.75 nm. We collected LIBS spectra of sulfur powder using the single pulse LIBS system and the seven channel spectrometer to use as a reference to compare to the steel samples. In figure 5, we show the spectra of the 4130 steel and the sulfur under argon. No sulfur emission is observed in the 4130 steel or any of the other numbered samples or standards.

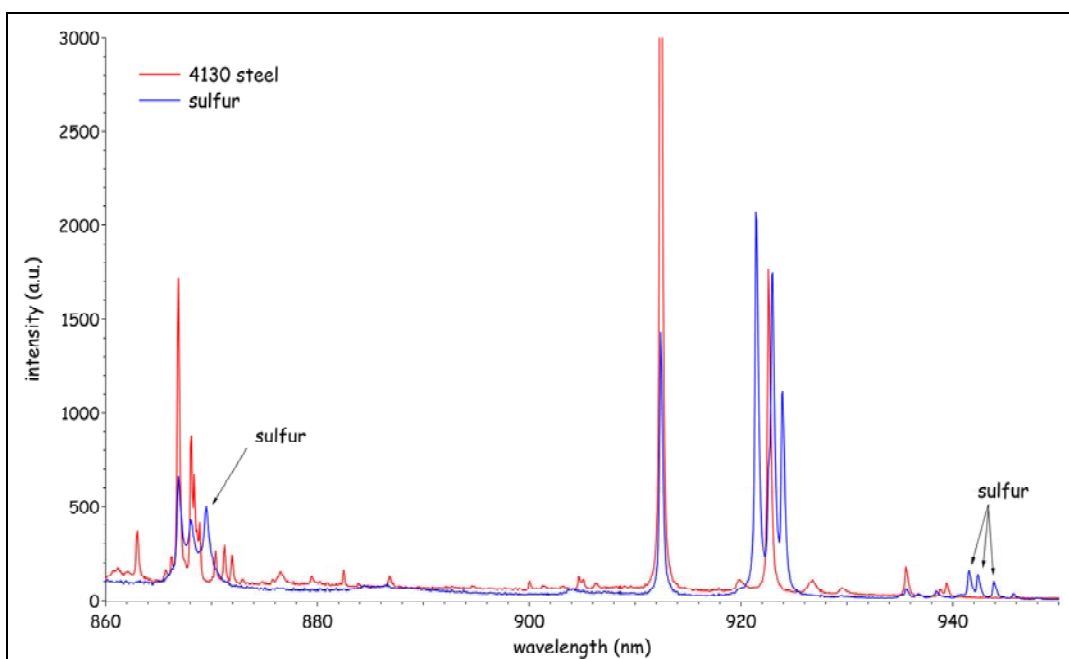


Figure 5. LIBS spectra of 4130 steel and sulfur powder.

## 4. Conclusions

As mentioned previously, the published literature for carbon and sulfur measurements in steel is conducted in the VUV (10, 11, 13, 15–18, 20). The advantage of using carbon and sulfur atomic emission peaks in this region is that the most prominent emission lines for carbon and sulfur are at 193.09 nm and 180.73 nm, respectively, compared to the lines used in the above study. They are also free of interference from the iron atomic emission lines, the most prevalent element in the steel samples. Successful calibration curves have been made in steel samples using these lines for sulfur and steel (10, 13, 17). The disadvantage of using these lines is air absorption in this region due to the O<sub>2</sub> Schumann-Runge band system. The light collection pathway and the spectrometers must be purged with inert gases (such as nitrogen or argon) in order to obtain usable signals. Optics and gratings capable of transmitting and dispersing VUV light must also be acquired. We were unable to observe any carbon or sulfur emission in any of the steel samples in the UV-VIS-NIR; however other trace elements such as titanium and chromium were detected. In order to detect carbon or sulfur in steel, LIBS spectra should be collected in the VUV emission range, which requires specialized equipment and a more complex experimental setup.

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## List of Symbols, Abbreviations, and Acronyms

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|           |  |
|-----------|--|
| ARL       | U.S. Army Research Laboratory                  |
| CCD       | charge-coupled device                          |
| EMCCD     | electron multiplying charge-coupled device     |
| LIBS      | Laser-induced breakdown spectroscopy           |
| NIST      | National Institute of Standards and Technology |
| UV-VIS-IR | ultraviolet-visible-near infrared              |
| VUV       | vacuum ultraviolet                             |

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